CONTAINER FORMED FROM MULTIMODAL ETHYLENE POLYMER

The present invention relates to containers comprising a composition based on multimodal ethylene polymer. It also relates to a process for manufacturing said containers and their use as bottles containing foodstuffs, and more particularly milk.

It is known to use polyethylene, and more particularly bimodal polyethylene, for

5 the manufacture of containers. For example, WO 01/14122 discloses large (>2L, preferably at least 30L) containers made from blow-moulded HDPE having a density of 945-960 kg/m^3 and MI$_{21}$ of 3-8 g/10min, and comprising bimodal HDPE made by first forming a high-density homopolymer and then forming a low-density copolymer, the high-density homopolymer comprising about 45-50wt% of the composition. US

10 6194520 discloses bimodal polymer blends suitable for blow-moulding typically having an MI$_{21}$ of at least 2 g/10min and a flow ratio (MI$_{21}$/MI$_2$) of at least 60. These are made by first forming a low-density block preferably comprising 45-50wt% of the composition and then the high-density block. Although blow-moulding into small bottles is mentioned, there is no discussion of the stiffness of the bottles.

15 EP 533160A discloses a bimodal polyethylene resin typically having a density of 945-980 kg/m^3 and MI$_{21}$ of 10-25 g/10min, comprising 10-35wt% of a homopolymer having a density of at least 960 kg/m^3 and an MI$_2$ of at least 30 g/10min ,and 65-90wt% of a copolymer having a density of less than 955 kg/m^3 and an MI$_{21}$ of 2-6 g/10min. The resin is said to have low haze, and is particularly suitable for films. There is no

20 disclosure of its use in containers, particularly not in small bottles.

Despite the above-mentioned disclosure relating to small bottles, commercially produced small bottles such as those for milk are currently typically made from monomodal polymers derived from a chromium or titanium catalyst. There is a

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continuing desire to reduce the weight of such bottles whilst maintaining the physical properties such as stress crack resistance and stiffness.

We have discovered a multimodal composition for bottles which provides improved stiffness compared with conventional bottles, and hence enables such a weight reduction. The compositions can also have an increased density without reducing the stress crack resistance, which permits improved processing.

Accordingly in a first aspect the present invention provides a container comprising a multimodal ethylene polymer having a standard density of at least 935 kg/m^3 and a fluidity index MI$_2$ of from 1 to 10 g/10 min, wherein said multimodal ethylene polymer comprises:

from 20 to 65 wt%, based on the total weight of the multimodal ethylene polymer, of a fraction comprising ethylene polymer (A) having a density of more than 950 kg/m^3 and a fluidity index MI$_2$ (A) of at least 10 g/10 min; and

from 80 to 35 wt %, based on the total weight of the multimodal ethylene polymer, of a fraction comprising a copolymer (B) of ethylene and at least one alpha-olefin containing from 3 to 12 carbon atoms, and having a fluidity index MI$_2$ (B) of less than 10 g/min and a content of said alpha-olefin(s) of 0.1 to 5 mol%.

Preferably the container is less than 2L in size, and preferably comprises a single layer of the above-defined polymer. However containers made of several layers of different resins, one or more or all of which is as defined above, are also within the scope of the invention.

It is also preferred that the amount of ethylene polymer (A) is from 30 to 40wt%.

A further aspect of the invention provides a container comprising ethylene polymer having a standard density of at least 935 kg/m^3, a fluidity index MI$_2$ of from 1 to 10 g/10 min, a Vicat point of at least 126.5°C and a resistance to slow cracking, measured according to ASTM D 1693 (1980), condition A of at least 60 hours. The ethylene polymer of this aspect of the invention is preferably multimodal.

By « multimodal ethylene polymer » is meant an ethylene polymer comprising at least two fractions having different fluidity indices (MI$_2$) so that it possesses a broad or multimodal molecular weight distribution. For the purposes of this invention, the term « multi-modal » need not necessarily be taken to mean that the GPC of the final multi-modal polymer exhibits two distinct molecular weight peaks.

The (multimodal) ethylene polymer used in the present invention has generally a

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standard density which does not exceed 965 kg/m^3. For the purposes of the present
invention, the standard density is measured according to the standard ISO 1183-3
(1999). The standard density preferably does not exceed 962 kg/m^3, more particularly
not 958 kg/m^3. The standard density is preferably at least 951 kg/m^3, more preferably at
5   least 955 kg/m^3.

We have found that small (<2L) containers of the invention have a stiffness as
measured by load at maximum load crushing which can be more than 10% better than
that of conventional bottles. Furthermore, they can be made at a higher density without
reducing the stress crack resistance. Higher densities are particularly valuable for the
10   long-life milk market, where it is necessary to sterilise the bottles with steam; a higher
density means that the sterilisation temperature can be raised, thereby shortening the
sterilisation period and increasing throughput. With monomodal polymers, such an
increase in density would result in poorer stress crack resistance. However the
compositions of the invention maintain excellent ESCR values even as the density is
15   increased.

The ethylene polymer used in the present invention preferably possesses a fluidity
index (MI$_2$) measured at 190°C under a load of 2.16 kg according to the standard
ASTM D 1238 (1998) of less than 4 g/10 min. MI$_2$ values of less than 2 g/10 min are
particularly preferred. The fluidity index MI$_2$ is at least 1 g/10 min, preferably at least
20   1.2 g/10 min. Fluidity indices of 1.4 to 1.8 g/10 min are particularly preferred.

Preferably the standard density of the ethylene polymer is at least 950 kg/m^3. It is
also preferred that the ethylene polymer used in the present invention has a molecular
weight distribution Mw/Mn of no more than 9. However it is preferably at least 5. The
ratio MI$_2$(A) /MI$_2$ is preferably from 5 to 200.

25   Preferably the standard density of the ethylene polymer (A) in the ethylene
polymer of the invention is more than 965 kg/m^3. The fraction of ethylene polymer (A)
is preferably at least 30% by weight compared with the total weight of the multimodal
ethylene polymer. The fraction of ethylene polymer (A) preferably does not exceed 45
wt%, more particularly it does not exceed 40 wt % compared with the total weight of
30   the multimodal ethylene polymer.

Correspondingly, the fraction of ethylene copolymer (B) in the multimodal
ethylene polymer is preferably at least 55%, more particularly at least 60 wt % by
weight compared with the total weight of the multimodal ethylene polymer. The

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fraction of ethylene copolymer (B) preferably does.not exceed 70 wt %.

The composition used in the present invention generally contains at least 95%, preferably at least 98 % by weight of the whole of the polymer (A) and the copolymer (B). Most particularly preferred is a composition consisting substantially only of
5   polymer (A) and copolymer (B).

Preferably, the polymer (A) is an ethylene homopolymer. For the purposes of the present invention, « ethylene homopolymer » means an ethylene polymer consisting mainly of monomer units of ethylene and substantially devoid of monomer units derived from other olefins. However polymer (A) may also be an ethylene copolymer with one
10   or more alpha-olefins containing from 3 to 12 carbon atoms.

By ethylene copolymer with one or more alpha-olefins containing from 3 to 12 carbon atoms (copolymer (B)) is meant a copolymer comprising monomer units derived from ethylene and monomer units derived from at least one alpha-olefin containing from 3 to 12 atoms of carbon. The alpha-olefin may be selected from among
15   olefinically unsaturated monomers such as butene-1, pentene-1, hexene-1, octene-1. Butene-1 is particularly preferred. The content of alpha-olefin in the copolymer (B) is preferably at least equal to 0.2 mol%, in particular at least equal to 0.3 mol%. The content of alpha-olefin in the copolymer (B) is most preferably no more than 4 mol%, and particularly no more than 3 mol%. Particularly good results are obtained with
20   alpha-olefin contents in the copolymer (B) of 0.5 to 2 mol%.

The standard density SD of the polymer (A) [SD(A)] is preferably at least 968 kg/m^3, more particularly at least 970 kg/m^3. Preferably, polymer (A) is characterised by an MI$_2$(A) of at least 30 g/10 min, more particularly at least 50 g/10 min. Preferably, the value of MI$_2$ (A) does not exceed 500 g/10 min, values of less than 400 g/10 min
25   being particularly preferred. Fluidity indices MI$_2$(A) of 80 to 200 g/10 min have given good results.

Copolymer (B) preferably has an MI$_2$(B) of at least 0.03 g/10 min, more particularly of at least 0.06 g/10 min. An MI$_2$(B) of at least 0.08 g/10 min is most preferred. The MI$_2$(B) preferably does not exceed 2 g/10 min, values of no more than 1
30   g/10 min being particularly preferred. Most preferred are MI$_2$(B) values of 0.08 to 0.8 g/10 min.

The multimodal ethylene polymer used in the present invention may be obtained by any suitable technique. It is possible, for example, to perform the mixing of polymer

(A) and copolymer (B) by any known process such as, for example, the molten mixing
of the two preformed polymers. The polymer may also be produced in a single reactor
using multi-catalysts to generate the different, desired polymer components. For
example polymer (A) would be formed using a catalyst with a sufficiently different

5   comonomer incorporation and molecular weight potential at given hydrogen and
comonomer composition in the polymerisation reactor to that of the catalyst used to
produce copolymer (B) such that the desired bi-modal or multi-modal polymer is
produced. The different catalysts selected may be co-supported, separately supported or
unsupported. Preferred, however, are processes in which polymer (A) and copolymer

10   (B) are prepared in at least two successive polymerisation stages. Whilst the polymers
may be produced in any order, it is particularly preferred that the preparation of polymer
(A) is performed first and then the preparation of the copolymer (B) in the presence of
the polymer (A) obtained from the first polymerisation stage. Preferably polymer (A) is
produced in the absence of any alpha-olefins containing more than 3 carbon atoms. The

15   polymerisation stages may each be carried out, independently of one another, in
suspension in an inert hydrocarbon diluent or in gaseous phase. A process comprising
at least two polymerisation stages in suspension in a hydrocarbon diluent is preferred.
The hydrocarbon diluent is generally chosen from among aliphatic hydrocarbons
containing from 3 to 10 carbon atoms. Preferably, the diluent is chosen from among

20   propane, isobutane, hexane or their mixtures.

In addition to the multimodal ethylene polymer, the composition used in the
present invention may contain conventional additives such as antioxidants, antacids, UV
stabilisers, dyes, fillers, antistatic agents and lubricating agents. The total content of
additives is typically 5 wt % compared with the total weight of the composition used in

25   the present invention. For white grade milk bottles for example, 1 or 4.5wt% pigment
(TiO2) is used.

The final composition used for the manufacture of containers according to the
invention may be obtained by any suitable known means. It is possible, for example, to
employ two successive stages, comprising first mixing the multimodal ethylene polymer

30   and where applicable the additives at ambient temperature, and then continuing the
mixing in the molten state in an extruder. The temperature of the second stage is
generally from 100 to 300°C, in particular from 120 to 250°C, more particularly from
about 130 to 210°C. An alternative method consists of introducing the additives and

where applicable the other compounds into the already molten multimodal ethylene polymer.

It is also possible to prepare initially a masterbatch comprising a first fraction of the multimodal ethylene polymer and any additives, the masterbatch being rich in

5   additives and optionally in other compounds. The masterbatch is then mixed with the remaining fraction of the multimodal ethylene polymer, for example during the manufacture of granules of the composition.

The containers according to the invention may be obtained by any known technique for the manufacture of objects. Extrusion blow-moulding, injection blow-

10   moulding and injection-stretch blow moulding are all suitable.

The examples which are described below serve to illustrate the invention. The meanings of the symbols used in these examples, the methods of measurement and the units of these quantities are explained below:

15   [A]: fraction of ethylene polymer (A) expressed in wt % compared with the total weight of the multimodal ethylene polymer.

[B]: fraction of ethylene copolymer (B) expressed in wt % compared with the total weight of the multimodal ethylene polymer.

MI_2: fluidity index of the multimodal ethylene polymer, expressed in g/10 min,

20   measured at 190°C under a load of 2.16kg according to the standard ASTM D 1238 (1998).

MI_2 (A): fluidity index of the ethylene polymer (A), expressed in g/10 min, measured at 190°C under a load of 2.16 kg according to the standard ASTM D 1238 (1998); in cases where the multimodal ethylene polymer is manufactured by a process

25   of two successive polymerisation stages, said value is measured on a sample of the polymer (A) taken from the first reactor.

MI_2 (B): fluidity index of the ethylene copolymer (B), expressed in g/10 min, measured at 190°C under a load of 2.16 kg according to the standard ASTM D 1238 (1998); in cases where the multimodal ethylene polymer is manufactured by a process

30   of two successive polymerisation stages, said value is calculated on the basis of the MI_2 and MI_2 (A) values.

SD: standard density of the multimodal ethylene polymer, expressed in kg/m^3, measured according to the standard ISO 1183-3 (1999).

SD (A): standard density of the ethylene polymer (A), expressed in kg/m^3, measured according to the standard ISO 1183-3 (1999); in cases where the multimodal ethylene polymer is manufactured by a process of two successive polymerisation stages, said value is measured on a sample of the polymer (A) taken from the first reactor.

5   SCB (B) : comonomer content of copolymer (B) as measured by the number of short-chain branches per 1000 C.

ESCR-A : resistance to slow cracking, expressed in hours, measured according to the standard ASTM D 1693 (1980), condition A, by immersion in an aqueous solution containing 10 vol% of nonylphenoxy-poly(ethyleneoxy)ethanol at 50°C, of a plate

10   obtained by compression of the composition used in the present invention according to the standard ASTM D 1928 (1980).

Stiffness: Empty bottles are crushed at 23°C at a constant speed (5mm/minute). The crushing machine measures the force needed to maintain the crushing speed, which depends on the degree of crushing. This crushing force curve has a maximum called the

15   Top Load, measured in N.

Vicat point (1kg load): According to ASTM 1525, the softening temperature of the resin is determined by measuring the temperature at which a specified type of needle loaded with 1kg can pass through the sample.

EXAMPLES 1-4

20   A composition comprising the following was blow-moulded using a Stork wheel machine into 1L bottles:

- 95.3 parts by weight of multimodal ethylene polymer manufactured by the same general process as disclosed in EP-A-603935;

- 4.5 parts by weight TiO$_2$ (for Examples 2 and 3 only);

25   - 0.05 parts by weight of calcium stearate;

- 0.05 parts by weight hydrotalcite ;

- 0.08 parts by weight Irganox B900.

The characteristics of the multimodal ethylene polymers used in the Examples are given in Table 1 below.

30   The characteristics of the bottles obtained are also given in Table 1 below. Example 1 was a natural colour resin -ie with no pigment- whilst Examples 2 to 4 were white.

EXAMPLES 5-6 (comparative)

Compositions were blow-moulded into bottles as in Examples 1 to 3, except that instead of the above multimodal polymer, a monomodal ethylene polymer also produced using a Ziegler catalyst was used, whose characteristics are given in Table 1 below. The other additives in the composition were identical. SEC analysis showed the

5   overall molecular weight distribution of these polymers to be very similar to those of Examples 1 to 4.

A comparison of Example 2 with Example 6 shows that the bottles according to the invention have a superior stiffness compared with those formed from monomodal polyethylene having a similar MI_2. This means that the bottles of the invention can be

10   made lighter without any loss of performance. Furthermore, the higher density of the bottle of Example 2 compared with that of Example 6 results in a higher Vicat point, which permits a higher sterilisation temperature to be used, resulting in shorter sterilisation times. With monomodal polymers, such an increase in density would result in poorer stress crack resistance. However it can be seen here that the ESCR values of

15   Examples 1-4 are substantially better than those of Examples 5 and 6.

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Table 1

Property	Units	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Type		Bimodal natural	Bimodal white	Bimodal white	Bimodal white	Mono modal natural	Mono modal white
MI_2	g/10 min	1.9	1.9	1.7	1.8	1.8	1.8
Flake SD*	kg/m^3	954.7	955	955	954.3	956.0	952.0
Mw			120005		103000	128280	120810
Mn			17103		13900	19092	21005
Mw/Mn			7.02		7.4	6.72	5.75
$MI_2(A)$	g/10 min	76.6	76.2	72.5	112.6	-	-
SD(A)	kg/m^3	970.1	969.6	970.1	970.2	-	-
$MI_2(B)$	g/10 min					-	-
[A]	wt %	35	35	35	30	-	-
[B]	wt %	65	65	65	70	-	-
SCB (B)	/1000C	1.6	1.6	1.6	1.6	0.3-0.5^	1.3-1.5^
ESCR-A	hour	71.4	61.9	71.7			25#
Stiffness: Top load	N		723				626.9
Vicat point	°C		126.7			127.3	125.5

* density of resin before addition of additives

^ value for whole resin

average value